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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements relating to Semicrystalline Glass and to the Coating of Metal therewith

We, PFAUDLER PERMITT, INC., of 1000 West Avenue, Rochester, New York, United States of America, a corporation organised and existing under the laws of the State of

5 New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to semicrystalline glasses, to methods of making them and, more particularly, to methods of applying them to metallic bases to form impervious coatings thereon having superior mechanical strength, impact and abrasion resistance, and high resistance to corrosion, oxidation and other forms of chemical attack.

It has been shown that partial crystallization of glass can be carried out under controlled conditions for the production of a semicrystalline material having a high strength, great erosion and abrasion resistance, and other properties superior to that of uncryallized or amorphous glasses.

The protection of metallic articles with a coating of glass or vitreous enamel has long been known. Such coatings exhibit all the desirable properties of glass. However, such coatings have limited resistance to abrasion, to thermal and mechanical shock, and to other mechanical stresses. The use of such coatings has been restricted to applications where the thermal or mechanical shock, abrasion or other such stresses were relatively low and where the superior corrosion resistance or other desirable properties of the glassy structure more than offset its disadvantages.

While such glass or vitreous enamel-coated objects have found wide use in the chemical industry because of their superior resistance to chemical attack, and more particularly their resistance to acids at high temperatures, their use has been restricted by the relative mechanical weakness, fragility

and vulnerability to mechanical and thermal shock of the coating.

It has now been found that the properties of glass may be considerably altered and improved by an incorporation of discontinuous or discrete non-glassy particles therein. Specifically, it has been found that strength and resistance to impact, thermal shock, and abrasion of glasses can be considerably enhanced by a controlled partial crystallisation or devitrification, which results in a material containing a proportion of a crystalline phase precipitated therein. These partially crystallised or devitrified glasses retain, in large measure, all the desirable non-reactive properties of the original glass itself. These improved glasses have exhibited great promise for the production of objects which are subjected to high and changing temperatures.

According to the present invention, a process of forming partially crystallised glass comprises the steps of making a crystallisable glass, producing a frit from the amorphous mass formed by melting the glass, reducing the frit to a powder, heating the powder to a temperature sufficient to cause the particles of the powder to coalesce, and maintaining the glass at a crystallising temperature to partially crystallise it.

The invention also consists in a partially crystallised glass which is formed from a crystallisable glass by melting the glass to an amorphous glassy mass, producing a frit from the amorphous mass, reducing the frit to a powder, heating the powder to a temperature sufficient to cause the particles of the powder to coalesce, and maintaining the glass at a crystallising temperature to partially crystallise the same.

The crystallized glasses, by their very nature, are extremely refractory and have high melting points. However, in order to apply a coating to a metallic base, it is necessary that the coating be fused in place in order to produce a smooth, adherent, uniform

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- coating covering the entire surface of the base and having no imperfections or pinholes which could serve as starting places for corrosive attack and subsequent failure of the base. It is, therefore, necessary to provide a coating material having a fusing or melting point below the maximum temperature to which the metallic base can safely be heated without warpage, oxidation, or other undesirable effects. This end is generally attained in the vitreous enamel industry by formulating the enamel to have a fusing point considerably below the maximum temperature to which the base can be heated.
- However, since crystalline coatings have a very high melting point, this is not always possible. For this reason, it is usually best to apply the coating composition to the metallic substrate in the amorphous or uncryallized form in which it is easily fusible in order to allow the glass composition to melt on the surface of the base to form an adherent uniform continuous glassy coating. The coated object is then subjected to a heat treatment cycle causing the glass to nucleate and crystallize *in situ*, producing a partially crystalline coating. By means of this technique, it is possible to produce an adherent, even, smooth coating on a metallic base, with the coating having a higher softening point than the parent glass itself. The provision of a method for applying an amorphous glass to the surface of a metallic base, and then subsequently subjecting the coated base to heat treatment cycle to cause the glass to nucleate and partially crystallize is another object of this invention.
- One important requirement in the vitreous enamel industry is the adjustment of the properties of the enamel so that it "fits" the object to be coated; that is, enamel must have a coefficient of thermal expansion which bears a definite relation to the coefficient of expansion of the base metal itself. When the enamel is applied to the base metal, and fired at high temperature, each particle of glass becomes less viscous and fuses to neighbouring particles, forming a thin layer covering the entire base. When the enameled base is cooled, the base metal begins to contract. As long as the enamel is in a plastic form, it can adjust to the change in dimension of the base and no stresses are set up. However, as the base metal enamel system is further cooled, it passes the point where enamel hardens or "sets" and can no longer accommodate itself to the change in dimension of the base. As the system further cools, both the base metal and the enamel continue to contract at a rate depending on their respective coefficient of thermal expansion. If the coefficient of thermal expansion of enamel and the glass were identical (which is never the case in practice), then no stresses would be set up as the base metal enamel system cools to room temperature. If the enamel should have a coefficient of thermal expansion smaller than that of the base metal (which is the usual case), it would tend to contract less rapidly and would be in compression when the system had cooled at room temperature. The magnitude of the stress depends on the difference in coefficients of expansion of the enamel and the base metal, on the "set point" of the enamel or the temperature at which the enamel is rigid enough to begin to take on stress and, to a lesser extent, on such properties as modulus of elasticity, and so forth. Thus, the enamel is generally subjected to stresses of considerable magnitude depending on the relationship between the coefficients of thermal expansion as described above.
- It is known that in order to produce a stable enamel coating on a metallic base, there are certain limits of allowable stresses for the enamel. Since glass of vitreous enamel is stronger in compression than in tension, it is desirable and, in fact, from a practical point of view, necessary to have the enamel in compression rather than in tension in the system at the temperature at which it will be used. The optimum magnitudes of these compressive stresses depend on the mechanical strength and modulus of elasticity of the enamel, the shape or configuration of the coated surface and the ultimate strength of the enamel.
- It has therefore, been found necessary to adjust the properties of the vitreous enamel to conform to the properties of the base metals to be coated so that a metal enamel system will be formed wherein the enamel will be subjected to compressive stresses within the allowable limits.
- The "fitting" of the coating to the base metal is also necessary in the case of coatings formed of partially crystallized glass, for the same reasons as described above in connection with enamel. However, in the case of partially crystallized glass, the variables controlling the coefficient of thermal expansion of the coating are more complex. In the case of crystallized coatings, not only is the total residual stress in the coating controlled by the initial composition, but also by the heat treatment which determines the size, composition and the amount of the crystals existing in the coating, and the composition of the residual glassy phase.
- The fact that the initial composition of the coating and the subsequent heat treatment can control the properties of the final crystallized glass coating renders it possible to control these properties as described above, and in addition renders it possible to provide coatings of varying properties on different portions of a single object. For example, it might become desirable to provide a coating having relatively high residual compressive

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- stress on the concave portions of a given piece of apparatus, and a coating having residual stresses of a smaller magnitude on the convex portions thereof.
- 5 Since the object of surface coatings is to impart corrosion or oxidation resistance, impermeability to gases, or other desirable properties to the base metal, it naturally follows that the coating must possess these properties in as great a degree as possible. Considerable progress has been made, for example, in devising formulae for glassy or vitreous enamel coatings which exhibit resistance to the corrosive attack of almost all acids, (except hydrofluoric) at almost all concentrations and other compositions have been developed which are also resistant to oxidation under a wide range of conditions. In order to have the crystallized glass coatings capable of serving under various environmental conditions, it is necessary that both components of the crystallized glass, that is, both the crystal phase and the residual glassy matrix, must have the desired properties.
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- The detailed nature of the invention will be apparent from the following description when taken in connection with the accompanying drawing, the single figure of which is a curve showing the stress existing in a layer of partially crystallized glass coating applied on a metallic base as a function of the temperature of the coated system.
- This invention is based, at least in part, upon the discovery that certain glass compositions may be crystallized, that the crystallization may be accelerated by the physical form of the amorphous glass, that the amorphous glass may be applied to metallic bases and crystallized *in situ* to form a polycrystalline-armorphous ceramic coating, and that the properties of the coating material may be adjusted with relation to the properties of the base metal and to the environmental condition of use to form coatings superior to those heretofore known.
- It is known that the mechanical strength, abrasion resistance, and other desirable properties of glasses can be greatly enhanced by controlled crystallization or devitrification. For example, U.K. Specification No. 829,447 discloses a semicrystalline ceramic composition comprising a continuous amorphous phase and a crystalline phase or phases evenly distributed throughout. Such crystalline phases are produced by controlled nucleation and subsequent devitrification of the glass composition, thereby growing the crystals *in situ*.
- In order to cause glasses to crystallize, it was heretofore considered necessary to include in the batch composition a so-called "nucleating agent" which is capable of separating from the batch in the form of nuclei, or very small crystals. In the aforementioned Specification No. 829,447 methods for forming glasses having substantial crystalline components are disclosed, with the use of titanium dioxide in substantial amounts as a nucleating agent. However, we have found that while titanium dioxide is effective as a nucleating agent, the presence of this material in the glass is not essential for the successful formation of partially crystallized glasses. A large number of glass compositions may be successfully crystallized if properly heat-treated although no titanium is present in the batch.

Table I, given below, sets forth a series of fourteen glasses, of which some contain titanium and others are titanium-free, which have been found crystallizable.

TAB. I
Composition (Percent by Weight) of Various Crystallizable Glasses

Table II, given below, shows a second group of twelve glasses which have been found suitable for crystallization. All of the glasses given below are titanium-free.

TABLE II
Composition (Percent by Weight) of Further Crystallizable Glasses.

Oxides	1	2	3	4	5	6	7	8	8	10	11	12
SiO ₂	62.5	62	61.5	62.43	62.5	62	62.5	62	64.5	63.9	66.3	65.7
Al ₂ O ₃	12.1	12	11.9	12.08	15.13	15	15.13	15	15.6	15.48	16.0	15.92
B ₂ O ₃	6.56	6.5	6.45	5.64	6.5	3.03	3					
Na ₂ O	4.03	4	3.97	4.02	4.03	4	7.56	7.5	7.8	7.74	8.02	7.96
K ₂ O	3.03	3	2.98	3.02								
Li ₂ O	9.08	9	8.93	9.07	9.08	9	9.08	9	9.37	9.28	9.64	9.56
CaO	1.51	1.5	1.49									
ZnO	1.21	1.2	1.19	1.21								
Cr ₂ O ₃		0.8	1.6	1.62		0.8		0.8		0.83		0.79
SrO					2.72	2.7	2.72	2.7	2.8	2.78		

5 In addition to the above, it is possible to crystallize glasses containing antimony, such as the following:

TABLE III

Oxides	Weight Percent
SiO ₂	58.8
Li ₂ O	7.5
Al ₂ O ₃	11.6
Na ₂ O	10.1
TiO ₂	6.1
MoO ₃	2.9
Sb ₂ O ₃	2.9

- 10 The heat treatment of these glasses may vary considerably depending upon the results to be obtained. For the majority of glasses, heating at 1200° to 2000°F. for from one to six hours is adequate for crystallization. For example, in a preliminary study involving glass rods of the above compositions, a double heat treatment was used involving a nucleation heat treatment in a temperature range of from 390°F. to 1200°F., for heating periods of from 17 to 165 hours. The subsequent crystallization temperature ranged from 1200°F. to 1525°F. for heating periods of from 2 to 17 hours. It was found with composition No. 1 (see Table I) that the maximum strength was obtained with a nucleation temperature of 750°F. maintained for a period of 162 hours and a subsequent 20
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- range of from 390°F. to 1200°F., for heating periods of from 17 to 165 hours. The subsequent crystallization temperature ranged from 1200°F. to 1525°F. for heating periods of from 2 to 17 hours. It was found with composition No. 1 (see Table I) that the maximum strength was obtained with a nucleation temperature of 750°F. maintained for a period of 162 hours and a subsequent 25

- crystallizing time of 4 hours at 1290°F. After this treatment, the average modulus of rupture of rods of this composition was 49,600 lbs. per square inch or approximately 4.6 times as great as the modulus of the same glass before heat treatment. The crystal phases present therein appear to be substantially betaspodumene plus Mg_2TiO_5 . These crystal compositions were obtained by X-ray diffraction methods, which merely indicate the presence of these phases and are not to be considered as precluding the existence of other crystalline phases in the glass.
- It was found that small amounts of crystal phases ranging from approximately 1% to approximately 5%, of a crystal size ranging from 500 angstroms to 10 microns produced the greatest increase in strength in the glass rods during experimental runs. However, these data are not proved to be completely applicable to similar compositions crystallized *in situ* upon a metal base, since the relative strength of the glass rods and impact resistance of similar crystallized coatings on metal substrates were not completely parallel. For this reason, the strength data obtained by study of experimental crystallized rods will not be further given, since this invention relates principally to the production of crystallized coatings on a metallic base.
- It is to be noted that quite a long time is needed for both the nucleation and the crystallizing heat treatments given above. It has been found that the use of such long heat treatment periods, including a lengthy nucleation treatment followed by a crystallization treatment, causes crystallization of all of the glasses in the above tables. However, when these glasses are applied to a metallic base, the heat treatments required to provide a substantially complete crystallization are considerably shorter. One explanation of this discrepancy is the fact that the crystallization or devitrification of glass appears to be a surface phenomenon related to the surface energy of the glass being treated. In other words, it appears that the crystallization initially takes place on the surface of the glass and gradually progresses inwardly into the body until, after an extended period of time, the entire glass is crystallized. Where the glass exists in a finely divided form as for application to a metallic base, each of the glass particles will begin to nucleate and to crystallize on the surface during the period when they are being heated to the fusion point for forming a continuous coating on the surface of the base metal. Moreover, as these glass particles approach the fusion temperature, they tend to "slump" or flatten out, which increases the surface area to volume ratio as the particles depart further and further from spherical configuration. During this period, the extended surface of the particle provides a large surface for the initiation of the crystallization. After the particles have coalesced to form a continuous coating, the large number of nuclei and crystals which have been initiated as described above are scattered throughout the body of the coating, thereby permitting crystallization to take place relatively quickly in order to produce a completely crystallized coating. For this reason, it has been found that many slowly crystallizing glasses, which would have very limited usefulness for the production of bulk articles of crystallized glass are nevertheless useful if the crystallization is initiated while the glass is in finely divided form as described above.
- Moreover, the understanding of this phenomenon provides a means for control of the crystallizing process by controlling the average particle size of the finely divided particles as applied to the metallic base. The finer the glass has been ground prior to the formation of the enamel slip for the coating process, the more rapid and complete the crystallization will be for any given heat treatment. Thus, it is possible to vary the degree of crystallization on any particular object to be coated by merely applying a more finely ground slip to the portions where accelerated crystallization is desired.
- Since one of the important end uses of partially crystallized glass coatings of the nature described herein is for the production of corrosion-resistant coated apparatus, the problem of the chemical resistance of the various phases of the coating upon exposure to commonly used reagents is of importance.
- In order to attack this problem systematically, samples of desirable mineral phases to be encountered have been subjected to corrosion tests in both the crystalline and amorphous states. The minerals were preferably first crushed and screened in order to provide samples having large relatively constant surface areas, in order to permit comparative evaluation of the corrosion resistance of the various materials.
- An example of a test which was found satisfactory for forming a basis for evaluating the phases to be considered in forming nucleated glass coatings according to this invention was carried out as follows: The samples to be investigated were crushed in an inert mortar and the crushed material transferred to a nest of sieves for separation. A uniform sample was taken having particles which passed through a 35 mesh sieve (No. 40) but remained on a 48 mesh sieve (No. 50), yielding a sample having particle size ranging from approximately 297 to 420 microns. These particles were then washed with alcohol in order to remove any mechanically adhering fines, and after careful drying, a sample was weighed out for the corrosion test itself. The corrosion test in one case comprised a treatment of the sample in

5 a 50 ml. of 0.02 N. sulphuric acid at 203°F. for a period of four hours. However, it is to be understood that the reagents and temperatures used for the test should be related to the reagents and other environmental factors which the coating will encounter in service. After the test, the decrease in the weight of the samples and the consumption of the sulphuric acid during the treatment were determined. The results are summarized 10 in the following table.

TABLE IV
Corrosion Test

Material	Amt. used in Test (gm)	RESULTS		
		Decrease in Wt. in %	Consumption of 0.02n H ₂ SO ₄ in ml/10 g.	Equivalent amt. of Na ₂ O in mg/10 g.
Rutile	3.3480	0.045	5.53	3.4
B Spodumene	3.0622	0.718	48.0	29.8
Glass Crystal	2.0630 1.9197	0.1115 0.0834	40.9 38.6	25.4 23.9
Li ₂ O Glass SiO ₂ Crystal	1.2445 1.2478	5.11 5.22	581 589	360 365
Li ₂ O Glass 2SiO ₂ Crystal	0.9617 1.4394	1.27 0.54	475 156	294 96.7

15 Although the above tests do not yield absolute corrosion rates for the materials tested, they do yield comparative data which permits the evaluation of various materials and gives sufficient indication to determine which are suitable for use in a particular environment. It is to be understood that these particular tests are given herein for the sake of example only, to show the steps which could be taken by anyone skilled in the art as part of the rational design of crystallized coatings for resisting any particular reagent or for any particular service. It is clear that if it is desired to design a coating for resisting other reagents, the steps to be followed would be equivalent to those outlined above. The resulting data would then be correlated with the other characteristics desired in the coating as herein explained, thereby permitting the logical choice of the materials having the largest over-all desirability for the purpose in question. 50

20 As stated above, the properties of the crystallized glass must be adjusted to "fit" the base metal to be coated in order to limit the stress in the glass to obtain the maximum durability and thermal and mechanical shock resistance. Since glass and ceramic material 55 in general, and crystallized glass in particular, are considerably stronger in compression than in tension, it is desirable that the residual stress be of compressive rather than a tensile nature. Further, it has been found through experience, both in the vitreous enamel art and by testing crystallized glass coatings, that magnitude of these stresses should lie between 8000 and 30,000 pounds per sq. inch (as measured by the techniques set forth below) and preferably in the range between 16,000 and 24,000 pounds per sq. inch for maximum durability and shock resistance. In order to successfully coat any particular base metal, it is therefore necessary to adjust the formulation and method of application of the coating to attain compressive stresses of the order of magnitude described above. It is clear that it is necessary to prepare different formulations for attaining the same stress on base metals of different natures. A formulation and method of application which would attain this end of a base of mild steel would not necessarily give desirable results on a different base metal such as, for example, stainless steel or one of the refractory metals. It is, therefore, necessary to adjust the formulation and method of application to suit each particular base metal. 60

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It has also been found that high compressive stresses are more desirable on concave surfaces than on convex surfaces. The compressive stress on a concave surface tends to force the glass against the metal, and improves the adherence and durability of the 80

- conting. On the other hand, high compressive stresses on convex portions actually tend to cause the coating to flake or splinter off the convex surface, and therefore, stresses of a smaller order of magnitude are desirable. On sharp convex surfaces such as flanges and the like, it is desirable that the compressive stress should not exceed 14,000 lbs. per square inch.
- 5 From the above discussion it can be seen that in order to rationally design a nucleated coating to "fit" a particular application, it is necessary to take into account the residual stress of the coating. In order to facilitate 10 the formulation of a satisfactory coating, it is therefore necessary to understand some of the factors entering into the final results and to be able to measure, in a quantitative fashion, the results of changes in formulae 15 made in accordance to the general rules which are herein described.
- There are two methods for controlling 20 the magnitudes of the stresses in the coating applied to a metallic base. The first method is adjustment of the formulation of the coating to obtain a material having the desired coefficient of expansion with relation to the metallic base, and the second is by adjusting the formulation to affect the "set point" of 25 the coating.
- The importance of the set point can be understood when it is appreciated that the coating is in a viscous semi-fluid condition 30 when it is fired on the metallic base. As the coated base is cooled, the coating can adjust to the changing dimensions of the contracting base metal as long as it remains in a viscous condition. However, at the set point, the viscosity of the coating becomes so great 35 that it cannot adjust to the contraction of the metallic base, and the formation of the stresses in the coating begins. The lower the set point of the coating, the nearer to room temperature the system can be cooled prior 40 to the initial formation of stresses in the coating, and the lower the final stresses in the coated base has reached room temperature. Thus, even in cases where the difference in 45 coefficient of expansion of the coating and the base metal differ markedly, if the coating has a low enough set point, the final stresses in the coating at room temperature may be relatively low since the stresses do not begin to build up until the coated article is relatively cool.
- 50 It has been found that the coefficient of thermal expansion of crystallized coatings depends mainly on the coefficient of expansion of the vitreous or glassy phase and only 55 to a smaller extent on the coefficient of expansion on the crystalline portion thereof. The coefficient of the glassy phase may be adjusted to varying the composition. For example, an increase in the proportion of sodium oxide in the glass causes an increase 60 in the coefficient of expansions with a resultant decrease in the compressive stresses in the final coating. The opposite effect has been attained by the increase in the percentage of boron oxides in the glass. A substitution of iron oxide for aluminium oxides decreases the residual stresses. Increases in the compressive residual stresses are caused by an increase in the proportion of lithium oxide, but in this case the crystalline portion of the coating is increased and this causes both an increase in the set point as well as a lowering of the coefficient of expansion.
- 65 The set point of the coating is also dependent on the melting point of the glassy or vitreous phase of the coating. An increase in the proportion of refractory oxide, such as aluminium oxides, silica, or magnesium oxides, would increase the temperature of the set point, and therefore tend to increase the residual stresses in the coating. Other refractory or high-melting oxides have, of course, a similar effect.
- 70 These principles can be used to advantage by any ceramist skilled in the art in order to adjust both the coefficient of expansion and the set point of the coating either upwardly or downwardly as desired to attain the coating to "fit" any given base. However, the understanding of the mechanism and the glasses and crystalline ceramics is not far enough advanced at the present time to permit theoretical prediction of the properties of the final glass or crystalline structure in an exact quantitative manner and therefore, a quantitative method for measuring the effects of adjustments of the formulation is required for the formulation of coatings having optimum properties for any particular base.
- 75 It has been found most convenient to measure the stresses existing in the base-coating system directly rather than to measure the coefficients of expansion, set points and the other factors separately and to calculate the final stress. For this reason, a procedure for carrying out this measurement quickly and efficiently in the laboratory will now be given.
- 80 A convenient apparatus for carrying out the measurement of the residual stress comprises a means for supporting one end of a thin strip of coated base metal, a controllable furnace, and means for measuring the deflection of the other end of the strip at various temperatures. For example, if a strip of the base metal in question is coated on one side with the formulation to be investigated and then cooled, the coating on the strip will be under compressive or tensile stress depending upon the composition of the coating. If the strip is thin enough, the compressed coating on one side will cause the strip to assume a curved position, the radius of this curve 85 depending on the degree of compression in
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- the glass. The principle of this instrument is similar to that of the bi-metallic strip commonly used for temperature measurements wherein a composite strip of two materials having different coefficients is subjected to a change of temperature. One of the materials will expand (or contract) to a greater degree than the other during the change in temperature, and the bi-metallic strip will assume a curved configuration with the material which has undergone the greater expansion being on the outside of the radius of the curve when the strip is heated. The thin strip of base metal coated with crystallized glass acts in a similar manner, with the coating acting as one of the metals in a bi-metallic strip. Thus, where a thin straight strip of the base metal being investigated is coated with a coating formulation, and slowly cooled, the strip begins to deflect as soon as the coating passes through its "set point." The magnitude of the stress in the coating can be calculated from a modulus of elasticity of the strip and the amount of deflection.
- As an example of this procedure, a specimen of 10-gauge steel, 6 inches long and 1 inch wide, was given a ground coating on both sides using a formulation very similar to that described in Table IX below. This ground coating was then fired on in the usual manner so as to obtain an equal coating on both sides of the specimen of a thickness of approximately 0.008 inches. After being ground coated, the centre 4 inches of one side of the strip was coated with the crystallized cover coat under investigation. The strip was then fired in an electric furnace to fuse the cover coating, and then cooled slowly to room temperature.
- The top end of the strip was then clamped in a vertical position in a controllable furnace, with the lower end hanging free. The furnace was then heated at a rate of approximately 8°C. per minute, and the deflection of the strip was measured. The deflections observed were then converted to stress in pounds per sq. inch. The results are shown by the curve in the drawing.
- Referring to the drawing, it can be seen that the stress at 120°F. was indicated to be about 18,000 lbs. per sq. inch. This stress decreased in almost a straight line as the temperature rose, since the base metal expanded more rapidly than the coating, thereby relieving the compressive stress in the coating. At a temperature of approximately 750°F. , the strip was substantially straight indicating that the stress in the coating material had been completely relieved and the coating was in a condition of zero stress. Further heating produced a reverse curvature in the strip indicating that the coating was now under tension, the base metal having expanded to such a degree that it was now actually longer than the coating. At approximately 900°F. , the strip began to straighten out again, and at a temperature of 1000° and above, the strip remains straight. This indicated that at approximately 900°F. the coating had begun to soften so that it began to conform to the dimensions of the base metal, thereby relieving the stress. The coating had completely softened at a temperature of approximately 1000° , so that no further stresses were possible above this temperature.
- It may be seen that by applying the above technique, the residual stresses in any base metal coating formulation system can be evaluated. By applying the technique described above, any starting formulation can be "fitted" by means of adjusting the thermal expansion characteristics and the set point of the coating so that it can be made to fit the particular base metal to be coated.
- To summarize the above, when the ceramist is required to formulate a coating for a given base metal to encounter particular service, it is necessary to proceed according to the steps outlined above. The first step is to evaluate the resistance to the given service environment of the various glass formulations and crystalline compositions. If such data is not available in the literature, it may be readily determined by standard laboratory corrosion testing techniques such as those described above in connection with the crystalline phases set forth. When it has been determined which crystalline phases and which amorphous glass formulations are resistant to the desired environment, the calculation hereinafter set forth can be used to determine the initial composition which will, upon nucleation, yield a coating having the desired crystalline phases in combination with the desired amorphous glassy matrix therebetween. Once this has been done, then the formulation is tested with the desired base metal for "fit" by the residual stress determining apparatus such as that described above. Should it be discovered that the residual stresses in the desired formulation do not fall within the desirable range given above, then adjustment may be made in the composition of the vitreous or glassy matrix according to either of the two principles described above. For example, if the stress is too low, it may be increased by increasing the proportion of a refractory oxide such as aluminium oxide or magnesium oxide in the formulation. Successive adjustment may be in both the set point and the coefficient of expansion of the glassy phase, until the residual stresses in the coating fall within the desired range. When this has been done, the formulation arrived at will be suitable for coating the base metal in question and will be suitable for the environmental conditions to be encountered. In connection with this, it might be pointed out that the formulation may be altered for use on different portions

- of the same object to be coated in order to have different residual stresses on portions of different configurations.
- The above technique can also be used to evaluate the heat treating cycle which results in the nucleation and crystallization of the glass to form a nucleated glass coating. For example, a rapid rise in temperature may result in fusing of the coating with the production of relatively few nuclei, while a slow rise in temperature may result in a fused coating containing large quantities of crystal nuclei in the glass. These conditions of heat treatment can be duplicated and studied in the laboratory and the results in terms of residual stresses can be studied by the techniques described above to arrive at satisfactory control of the final process prior to full scale production.
- A better understanding of the application of the above mentioned principles and methods can be most clearly obtained by reference to the following example:
- For purposes of illustration it will be assumed that it is desired to apply to mild steel a coating resistant to boiling hydrochloric acid. Certain criteria which the coating will have to meet are as follows:
- (a) Since the coating is to be applied to mild steel, the firing temperature should not exceed approximately 1600°F., because higher firing temperatures are apt to cause warpage and excessive oxidation of the base metal.
- (b) The compressive stresses should be approximately 12,000 to 16,000 pounds per square inch at room temperature, and the coefficient of thermal expansion of the coating must be adjusted to give these values on mild steel.
- (c) The acid resistance to boiling hydrochloric acid should be good. As a practical criteria, the corrosion should not exceed 30 to 40 mils per year in boiling 20% hydrochloric acid in the vapor phase.
- (d) In order to meet commercial standards, the thermal shock resistance should be approximately 450°F. This means that the coating should be able to withstand being heated, and cooled through a range of 450°F. by a water quench without showing any signs of cracking or crazing.
- The first step in approaching a problem of this nature is to select a residual glass which has properties which are similar to the requirements of the coating, and which would be affected by the various crystal phases in such a way as to give the needed properties. For example, the residual glass should have a higher coefficient of thermal expansion than desired for the final coating since the precipitation of crystalline phases having relatively small coefficients of expansion such as for example, beta spodumene will considerably reduce the same. Therefore, initially, a glass composition having approximately 75% the desired compressive stress on mild steel at room temperature is a good starting point for the formulation of such a glass.
- Many glass compositions are given in the literature, and any glass having a suitable coefficient of expansion and chemical resistance could be selected as a starting point in this project. It has been found for example that the following composition would be suitable for this purpose.

TABLE V

Oxides	Wt. Percent
SiO ₂	65.0
Na ₂ O	11.0
B ₂ O ₃	9.0
TiO ₂	5.0
SrO	3.0
Li ₂ O	7.0

- When this glass composition is smelted, and reduced to a powder, applied to a base metal disc, and subjected to 20% hydrochloric acid in the vapour phase at the boiling point, it was found that the corrosion rate was approximately 16.5 mils per year. Since this is well within the criteria set forth above, this glass is suitable for the residual glassy or amorphous phase of the coating from a corrosion resistant standpoint.
- It was assumed, as a starting point, that it is desirable that approximately 50% of the polycrystalline-amorphous ceramic coating should comprise the residual glass composition, and approximately 50% should be in the crystalline phase. This assumption is

- based on the estimate that a larger percentage of the crystalline phase would probably result in a firing temperature higher than could be tolerated within the criteria described above for a coating of mild steel. Accordingly, these proportions have been used as initial percentage for calculating the formulations.
- In the selection of the crystalline phase, it is necessary to run corrosion tests on the crystalline phases which are intended to be used. In certain cases, as with well-known minerals such as rutile, beta spodumene, and the like, this data is available in the literature; if it is not, this data must be obtained in the laboratory by the methods herein outlined. In any case, the selection of the crystalline phases should be such that the corrosion resistance which is the end result desired in such a coating is not significantly degraded by the addition of this phase.
- In this particular case, it was found that beta spodumene and lithium titanium silicate have relatively good corrosion resistance when exposed to hydrochloric acid. The coefficient of thermal expansion of lithium titanium silicate is approximately 8.6×10^{-6} , which is considerably larger than that of beta spodumene, whose coefficient is very close to zero. Thus, in order to avoid severe changes in the coefficient of expansion of the finished coating, 30% of the total coating weight is composed of lithium titanium silicate and 20% of beta spodumene.
- Having made these preliminary decisions, it is then necessary to calculate the starting weight of the ingredients to be added to the glass so that, if the crystal phases come out as desired, the residual glass composition will be that given in Table V. A sample calculation follows:
- Since the formula of beta spodumene is $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, the weight percent of each of the following oxides in lithium titanium silicate is given in Table VI. Each of the weights is multiplied by 0.20 since this constituent will be 20% of the finished coating, to give the total weight percent of each of the oxides and the total coating composition necessary to cause 20% of beta spodumene to crystallize.

TABLE VI

Oxide	Wt. Percent	Wt. Percent of total coating comp.
Li_2O	$8.03 \times .20 =$	1.61
Al_2O_3	$27.30 \times .20 =$	5.46
SiO_2	$64.60 \times .20 =$	12.92

By similar calculation for lithium titanium silicate, $\text{Li}_2\text{O} \cdot \text{TiO}_2 \cdot \text{SiO}_2$, the weight percents in the total coating composition necessary to crystallize 30% of lithium titanium silicate are given in the following table:

TABLE VII

Oxide	Wt. Percent	Wt. Percent of total coating comp.
Li_2O	$17.55 \times .30 =$	5.27
TiO_2	$47.00 \times .30 =$	14.10
SiO_2	$35.35 \times .30 =$	10.60

Adding the oxide percentages given in Tables VI and VII above, together with 50% of the oxide percentages given in Table V,

TABLE VIII

Oxide	Wt. Percent of Total Coating Comp.
SiO ₂	56.02
Na ₂ O	6.50
B ₂ O ₃	4.50
TiO ₂	16.60
SrO	1.50
Li ₂ O	10.38
Al ₂ O ₃	5.46

The object to be coated, for instance a vessel of fabricated mild steel, is first prepared in the usual way for porcelain enameling. The surface is first thoroughly cleaned and sand blasted to remove all traces of foreign matter, scale, and the like which could interfere with the adhesion of a subsequently applied coating. The clean and sand blasted base is then given a coat of ground-

coat enamel in the usual manner. This ground-coat enamel is especially formulated to produce an adherent bond with the base metal in order to bond the subsequent corrosion resistant cover coats securely to the object to be coated. A typical formula for enamel ground coat suitable for use for this purpose is as follows:

TABLE IX

Oxides	Weight Percent
B ₂ O ₃	16.0
Na ₂ O	14.7
K ₂ O	4.4
SiO ₂	48.5
Al ₂ O ₃	6.4
CaO	4.0
F ₂	3.7
Co ₃ O ₄	0.6
MnO ₂	1.7

The above materials are smelted to form a homogenous glassy material, which is generally reduced to a coarse frit by being poured into cold water. The resulting granulated mass is then ground in water together with various mil additions to form an "enamel slip" which is a thin liquid approximating the consistency of paint. This liquid is then applied to the surface to be coated by spraying, dipping, slushing or any other of the known enameling techniques. The coated surface is then dried and fired at a tempera-

- ture of approximately 1600°F. for approximately 30 minutes. This firing process causes the particles of enamel to fuse and to adhere tightly to the base metal to form a uniform glassy coating thereon. This procedure as herein described is known, and forms no part of this invention. 70
- When the ground coat has been applied as described above, the object is ready for receiving its cover coat of the formulation set forth in Table VIII. 75
- After the formulation has been made up as described above, the components are smelted to form a glassy composition. This glassy composition is then fritted by being quenched in water (or dry quenched) in order to reduce it to the granular state. At this stage in the process, the coating material is completely amorphous, and to all appearances is identical with the known types of vitreous enamel. 80
- The above frit is then dry milled or wet milled depending on whether it is to be applied by dry or wet processing techniques. If the frit is wet milled, it is reduced to a thin paint-like suspension suitable for the application to a surface by spraying, dipping or the like. If the material is dry milled, it is reduced to a fine powder which may be dusted upon the hot surface. The coating 85
- is then fired at a temperature which varies with the viscosity of the glass, but would, in the case of the formulation given in Table VIII, be in the range of from 1400°F. to 1700°F. The heating rate of the coating is important at this point since it will have a substantial effect on the rate of crystallization of the coating. Should the heating rate be too slow, there is a danger that the coating might crystallize and become refractory prior to proper fusion. If this should happen, the coating would never attain the thin flowable stage which is necessary in order to provide a uniform glossy continuous coating on the object to be fired. On the other hand, if the heating rate is too fast, the coating may become too fluid during this stage of the cycle and could produce runs or sags in the finished product. 90
- It has been found that a certain amount of crystallization during initial firing of the crystallizable glass coating can be beneficial since it will reduce the necessary time required for further heat treating. This partial crystallization or nucleation which occurs during this stage of the cycle is similar to and can be controlled in a manner similar to that which occurs during subsequent heat treatment. For this reason, the rate of firing during the initial fusing should be considered as part of the total nucleating heat treatment process, and subsequent heat treatment must be adjusted to take account of the rates of firing occurring during the initial fusing of the coating. However, should this prove to be undesirable, it is possible to fire the coating 95
- at temperatures which will keep it in the completely glassy or amorphous stage, and then nucleate the crystals at a somewhat lower temperature (approximately 1100°F.) and then heat treat to obtain the desired crystal structure in the coating. 100
- After the coating has been applied and fused as described above, it is then subjected to a heat treating cycle for crystallizing the coating. The heat treatment of compositions such as those set forth above on a mild steel base will generally range from a temperature of 1300°F. to 1600°F. for periods of from 1 to 3 hours. The temperature and duration of this treatment is limited by the resistance of the base metal to oxidation. However, if it should be necessary, this treatment could be carried on under a non-oxidising atmosphere to prevent any deterioration of the base metal during longer heat treatment times. 105
- It has been found that a treatment such as that described above will yield a coating containing many small crystals ranging from sub-microns to 100 microns (with the bulk being under 1 micron) in size uniformly dispersed throughout the glassy matrix. Such a coating properly crystallized has a mechanical strength (as measured by bending tests of crystallized glass rods) of three to over four times of that of the uncrystallized or amorphous glass. 110
- The coefficient of linear expansion of a coating such as that described above, would range from approximately $7.5 \text{ to } 11.0 \times 10^{-6}$ inches per inch per degree Centigrade. As described above, this can be adjusted by small compositional changes in order to fit the particular metal but the above range has been found generally satisfactory for coating mild steel bases. However, the coefficient of linear expansion is not the ultimate test since, as described above, the set point of the coating has also considerable effect on determining the magnitude of the stress of the finished coating base metal. For this reason the fitting of a composition to any particular base metal should be done by use of the stress measuring techniques herein described. 115
- It is to be emphasized that the percentages given above are not absolute percentages suitable for all purposes. If substantially all of the crystallizable elements crystallize to form the crystalline phases defined above, the residual glassy phase would contain oxides as shown in Table V. However, although these percentages are not absolute, it has been found, by X-ray diffraction and other measuring means, that the crystalline phases approach those given in Tables VI and VII. 120
- The physical properties of the polycrystalline glass as formed in the above example have been measured and compared with the properties of similar glass prior to the crystallization. It has been found that the abrasion resistance is significantly increased, ther- 125

mal shock resistance is substantially increased, and the refractoriness of the material is greatly increased. The mechanical strength (as measured by bending tests) is also increased. The corrosion resistance is slightly decreased but this effect can be controlled by a proper choice of composition, resulting in desirable corrosion resistant crystalline phases and a desirable corrosion resistant residual glass composition.

It is clear that the above formulation satisfies the initial criteria set forth above, and constitutes a satisfactory coating for mild steel apparatus intended to be exposed to the corrosive attacks of hydrochloric acid. However, should such a coating prove unsatisfactory in any respect, or should it be desired to adapt a similar coating for use on a different base material, whether metallic or non-metallic, the application of the principles set forth above clearly indicate the modifications which must be made.

As pointed out above, the coatings on convex surfaces of small radii should have smaller residual stresses. To this end, it is often desirable to alter the composition of the coating for the application to different parts of the same article. For example, it may be desirable to coat the inside of a large piece of chemical processing apparatus with the coating of one formulation and to apply the coating of somewhat modified formulation to convex radii of the nozzles, flanges and other fittings. Moreover, when coating large pieces of apparatus of complex shape, the coating on certain parts of the apparatus may contain a greater proportion of crystals than others due to differential heating effects. For example, massive portions of the apparatus to be coated may be brought to crystallizing temperatures more slowly than the smaller portions, and this difference in the heat treatment of various parts of the same apparatus may result in diverse properties of the coating on these various parts. This effect may be corrected by applying coatings of different compositions to various parts of the same apparatus in order to attain the most desirable over-all properties in the coating over the entire surface being coated.

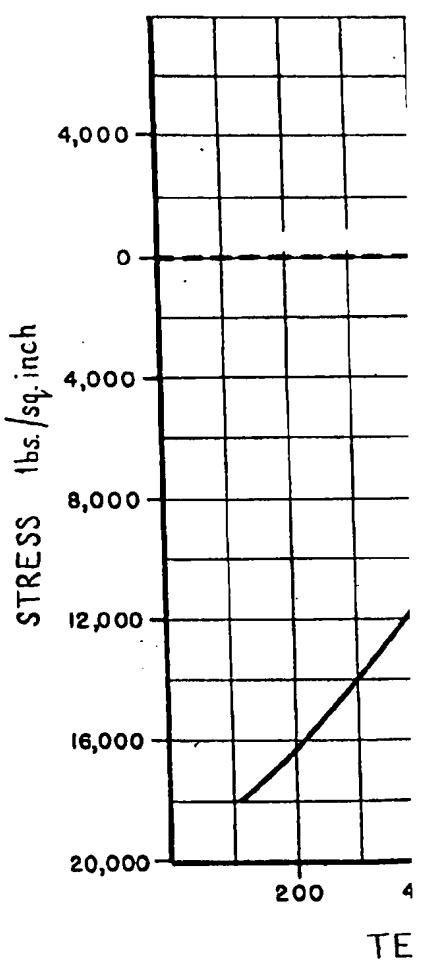
The foregoing example is intended to be illustrative of the methods of applying the principles broadly set forth herein. Obviously, anyone skilled in the ceramic or glass making arts, could apply the teaching set forth above to formulate a coating to fit any base, and, within the limits set by the available materials, to perform any desired service. In particular, other crystalline phases such as beta eucryptite, rutile, brookite, lithium metasilicate, lithium disilicate, sphene, crystobalite, Mg_2TiO_5 , Mg_2TiO_4 and Mg_2TiO_3 , have proven satisfactory for various purposes.

WHAT WE CLAIM IS:

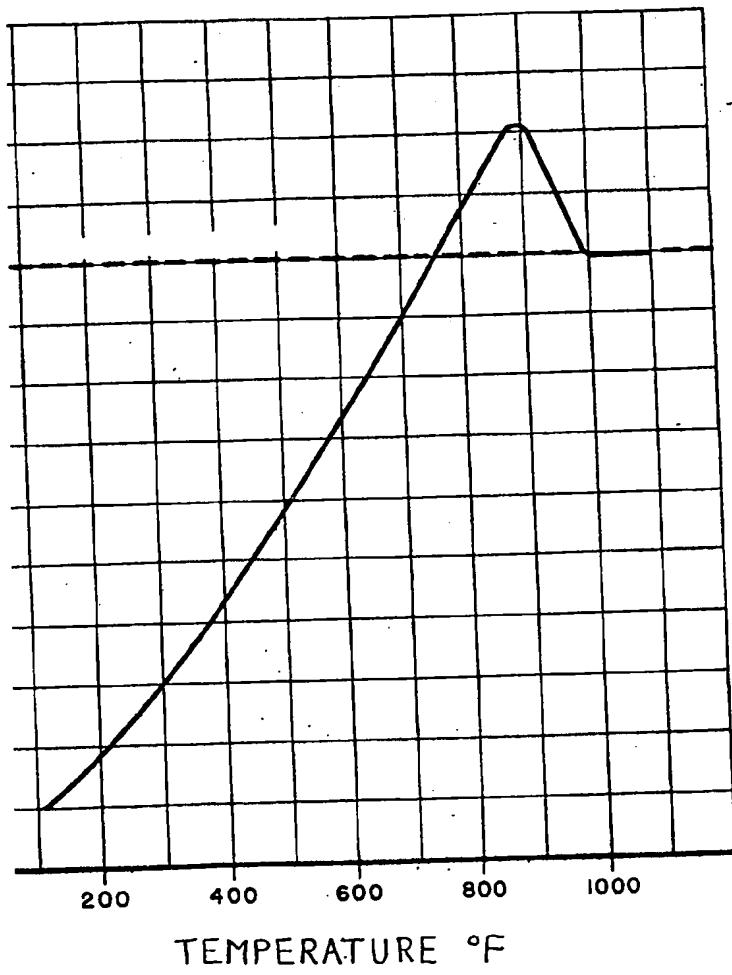
1. A process of forming partially crystallized glass, comprising the steps of making a crystallisable glass, producing a frit from the amorphous mass formed by melting the glass, reducing the frit to a powder, heating the powder to a temperature sufficient to cause the particles of the powder to coalesce, and maintaining the glass at a crystallising temperature to partially crystallise it. 65
2. A process as claimed in claim 1, in which, after the frit has been powdered, the powder is maintained at a nucleation temperature to cause the formation of crystal nuclei therein and is subsequently maintained at the temperature sufficient to cause the particles in the powder to coalesce but insufficient to destroy the nuclei therein, before it is maintained at a crystallising temperature. 75
3. A process as claimed in claim 2, in which the nucleation temperature ranges from 800°F to 1200°F. 85
4. A process as claimed in claim 1, 2 or 3, in which the crystallisable glass comprises from 40% to 70% silica and from 10% to 25% of an alkali metal oxide. 90
5. A process as claimed in claim 4, in which the crystallisable glass also contains one or more of the oxides; TiO_2 , CeO_2 , MnO_2 , ZrO_2 , Al_2O_3 , B_2O_3 , Sb_2O_3 , Cr_2O_3 , Fe_2O_3 , CaO , ZnO and SrO . 95
6. A process as claimed in claim 5, in which the crystallisable glass contains from 0% to 20% Al_2O_3 . 100
7. A process as claimed in any preceding claim, in which the particles of the powder are of such a size that no more than 15% thereof is retained on a 200 mesh screen. 105
8. A process as claimed in any preceding claim, in which the crystallising temperature ranges from 1200° to 2000°F. 110
9. A process as claimed in claim 8, in which the glass is maintained at the crystallising temperature for 1 to 6 hours. 115
10. A process as claimed in claim 9, in which the crystallising temperature ranges from 1300° to 1600°F and is maintained for one to three hours. 120
11. A process of forming partially crystallised glass as claimed in claim 1, substantially as hereinbefore described. 125
12. A process of coating a metallic article with a partially crystallised glass prepared according to the process of any of claims 1 to 11, in which the powder is applied to the metallic article before heating to the temperature at which the powder coalesces and the powder-coated article is heated to the coalescing temperature and then to the crystallising temperature to partially crystallise the glass as a coating on the article. 120
13. A process as claimed in claim 12, in which the composition of the crystallisable

- glass is chosen so that the partially crystallised glass is resistant to given environmental conditions, by selecting a glass composition resistant to such environmental conditions, 5 selecting one or more crystalline phases resistant to these environmental conditions, and calculating an initial glass formulation which when subjected to crystallising temperatures yields a coating having the desired crystalline phases dispersed in a matrix of resistant glass.
- 10 14. A process as claimed in claim 13, in which the crystallisable glass has a coefficient of expansion and a set point such that when applied to the article and crystallised thereon it is subjected to a residual compressive stress of from 8000 to 30,000 lbs per square inch.
- 15 15. A partially-crystallised glass, which is formed from a crystallisable glass by melting the glass to an amorphous glassy mass, producing a frit from the amorphous mass, reducing the frit to a powder, heating the powder to a temperature sufficient to cause 20 the particles of the powder to coalesce, and maintaining the glass at a crystallising temperature to partially crystallise the same.
- 25 16. A partially-crystallised glass as claimed in claim 15, in which the powder is of a fineness such that no more than 15% thereof is retained on a 200 mesh screen.
- 30 17. A partially-crystallised glass as claimed in claim 15 or 16, in which the crystals comprise one or more of: beta-spodumene, 35 beta-eucryptite, lithium titanium silicate, rutile, brookite, lithium metasilicate, lithium disilicate, sphene, crystobalite, Mg_2TiO_5 , $MgTiO_3$ and Mg_7TiO_8 .
- 35 18. A partially-crystallised glass as claimed in claim 17, in which the crystals comprise less than 50% by weight thereof.
- 40 19. A partially-crystallised glass as claimed in claim 15, 16, 17 or 18, comprising from 40% to 70% silica, and from 10% to 25% of an alkali metal oxide.
- 45 20. A partially-crystallised glass as claimed in claim 19, which also contains one or more of the oxides: TiO_2 , Al_2O_3 , CeO_2 , MnO_2 , ZrO_2 , B_2O_3 , Fe_2O_3 , Sb_2O_3 , Cr_2O_3 , CaO , ZnO and SrO .
- 50 21. Partially-crystallised glass, when made by a process according to any of claims 1 to 11.
22. A metal article coated with a coating of a partially-crystallised glass as claimed in any of claims 15 to 20, in which the powder is applied to the metal article before heating to the temperature at which the powder coalesces.
- 55 23. A coated article as claimed in claim 22, in which the largest dimension of the crystals is smaller than 100 microns.
24. A coated article as claimed in claim 22 or 23, in which the coating is under a compressive stress from 8,000 to 30,000 lbs per square inch.
- 60 25. A coated article as claimed in claim 22 or 23, in which the coating on the concave curved portions of the article is under a compressive stress of from 15,000 to 30,000 lbs per square inch and the coating on the convex portion of the article is under a compressive stress from 8000 to 30,000 lbs per square inch.
- 65 26. A metal article coated with a coating of a partially-crystallised glass, when made by a process according to claim 12, 13, 14 or 15.

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